

INVESTIGATIONS OF THE HYDROCARBON STRUCTURE OF KEROGEN FROM
OIL SHALE OF THE GREEN RIVER FORMATION

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I. INTRODUCTION

Colorado Oil Shale of the Green River Formation contains about 16 per cent insoluble organic matter, the so-called "kerogen." This represents about 80 per cent of the total organic matter present. The remaining 20 per cent soluble organic matter represents the "soluble bitumen."

The problem of the nature and constitution of both "kerogen" and soluble bitumen and their relationship to each other is of considerable interest both with respect to the question of the origin, genesis and geochemistry of oil shale and the problem of degradation mechanisms during pyrolysis.

The paper discusses investigations on the structure of kerogen conducted at the Center for Fundamental Oil Shale Research of the University of Denver. Among several approaches for the structural elucidation of oil shale kerogen investigated to date, the MPCM-method developed at the Center proved most effective.

By using the combination of micro-pyrochromatography and mass spectrometry it could be shown that "kerogen" consists of a three-dimensional organic matrix of high molecular weight. The hydrocarbon portion of the matrix itself appears to consist of polycyclic "protokerogen" subunits or nuclei (of tetralin, terpenoid, phenanthrenoid and steroid type structure) interconnected by long chain alkanes and isoprenoids to form the three-dimensional network of the kerogen matrix. Studies on synthetic model compounds of the "protokerogen" type support this concept.

However, the matrix of "kerogen" in the conventional term also contains a substantial amount of entrapped long chain alkanes, normal and branched fatty acids and other uncondensed "protokerogen" subunits not removed by the normal extraction process. The presence of these compounds, which appear to have been overlooked, may considerably influence the results of structural investigations reported in the literature.

Morphological and physicochemical studies also indicate that Green River Oil Shale contains at least two major types of kerogen: alpha-kerogen and beta-kerogen. These are probably of different origins.

The chemical structure of the protokerogen subunits identified by macropyrolysis, chemical cleavage and by the MPCM-method used in conjunction with reaction chromatography are described. The possible relationship between kerogen structure, the soluble bitumen and the biogenesis and geochemical origin of oil shale are discussed.

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II. MATERIALS AND METHODS

A. Oil Shale Samples.

Samples were taken from freshly mined raw shale of the Green River Formation which were part of a 100 ton lot from the underground room-and-pillar mine of the Colony Development Corporation in the East Middle Fork of the Parachute Creek in Colorado. The material was crushed to - 1/4 inch size and riffled. Samples used for the extraction, separation and analysis experiments were ground to -100 mesh.

B. Extraction of Soluble Bitumen.

The ground raw shale was exhaustively extracted by percolation at 50°C with a number of organic solvents with successively increasing polarity over several weeks. This was followed by treatment with acetic acid to remove inorganic carbonates and liberate any weaker acids present. The acid leached material was again exhaustively extracted with the same solvent sequence.

C. Concentration of Kerogen.

Two methods were used for the separation of kerogen from the inorganic matrix:

1. Density gradient separation and 2. Chemical Separation by Acid Leaching. The density gradient method yielded a kerogen concentrate with about 3 percent ash content. However, the yield was rather low. The acid leaching method gave a concentrate with about 12 percent ash content. This material was used during most of the preliminary investigations.

D. Analytical Methods.

A number of different approaches were investigated for the degradation of kerogen to larger but tractable and identifiable fragments. Among these the most promising one was a combination of micro-pyrolysis with pyrochromatography and mass spectrometry, designated as the MPCM method. A schematic outline of this method is shown in Figure 1.

This controlled pyrolysis method combined with reaction chromatography and mass spectrometry was used successfully for the separation and identification of predominantly primary pyrolysis fragments. Such fragments can be identified and yield useful information for the evaluation of the structure of kerogen subunits and that of kerogen itself.

III. PROCEDURE

A modified "Fischer Technik" Induction Micro Pyrolysis instrument was used. This unit could be operated either in conjunction with a condenser unit or with a GC-MS unit consisting of a Beckman GC-4 unit and a AEI Model MS 12 mass spectrometer. The kerogen concentrate was applied to the pyrolysis needles in the form of a very thin coating. The needle was paced into a micro pyrolysis chamber equipped with a injection syringe tip which was inserted into the injection port of the GC instrument or into a micro-condenser unit. After ignition the volatile material was analyzed directly by the GC-MS unit or collected in the condenser for pre-separation of major fractions. To obtain sufficient material for the latter procedures e.g. GPC or micro column chromatography, up to 200 individual pyrolysis reactions had to be carried out. The pre-fractionation scheme used is shown in Figure 2. Some of these fractions (in particular the neutral hydrocarbon fractions) were subsequently analyzed by the GC-MS method.

Similar pyrolytic fragmentation experiments were carried out in conjunction with reaction chromatography using either selenium dehydrogenation or hydrogenation reactions. In this way one obtains either aromatized or completely saturated derivatives of the primary pyrolysis fragments; most of them representing "protokerogen" moieties.

Comparison of these derivative structures with the original primary fragments using these methods allows a better structural evaluation of the subunits of the hydrocarbon matrix of oil shale kerogen.

The pyrolysis fragmentation pattern of major subunits obtained by the MPGM method and the mass spectral fragmentation patterns of a number of such subunits could be corroborated using identical or closely related synthetic reference compounds.

IV. DISCUSSION

The results of these studies carried out over a period of several years led to the following conclusions:

1. Microscopic analysis and micro-spectrophotometric analysis of isolated "kerogen" particles indicates the presence of at least two types of kerogen components in the oil shale of the Green River Formation: The major component (designated as alpha-kerogen), represents an alginite like material of low aromatic content; the second component is present in the form of darker reddish-brown particles (beta-kerogen) with a much higher content of aromatic (probably polycondensed) material. The latter represents about 5 percent of the total kerogen present.

2. Under controlled micropyrolysis alpha-kerogen yields several types of subunits:

- a) normal and branched alkanes,
- b) alkyl derivatives of decalins and tetralins, (mostly o-substituted) and
- c) alkyl substituted tricyclic terpenoid or phenanthrenoid type derivatives.

In addition there are present a smaller number of higher molecular weight ring-compounds of probably steroid origin.

Some of the major subunits obtained by the MPGM method are summarized in Table I.

3. From these subunits and others obtained by micro-pyrolysis from kerogen one can rationalize a number of possible aspects concerning the structure of alpha-kerogen:

- a) The hydrocarbon part of the kerogen appears to be relatively uniformly structured i.e. consisting of nuclei of subunits (representing built-in "protokerogen" units), interlinked by normal or branched alkane bridges or long chain ether bridges. The major part of the subunits consist of alkyl substituted decalins or tetralins. A smaller proportion of these subunits may consist of ring systems containing hetero atoms.
- b) The bulk of the skeleton is hetero structural i.e. several hundred different types of subunits form a three-dimensional organic matrix. However there are repeatedly occurring predominant subunits of two and three-membered ring-systems. These have characteristic structural features which may be very informative about the origin of the "protokerogen" subunits. Thus the kerogen of the Green River Formation does not represent a material of randomly connected carbon atoms (scrambled eggs) but appears to be structured.
- c) One can make an attempt to put the principal subunits together and thus arrive at some reasonable reconstructed original structure of the kerogen molecule. From the structure of the subunits obtained it appears that they were interlinked by di- and tri-substituted subunits. The structure of the hydrocarbon skeleton of kerogen could therefore be visualized by a generalized structure shown in Figure 3.

4. A somewhat anomalous phenomenon observed in isolated kerogen concentrates provided additional information on the possible structure of kerogen. Exhaustively extracted kerogen stored under nitrogen for two years, yielded upon re-extraction with n-hexane 5-6 percent of material which upon analysis proved to be a mixture of normal and branched saturated hydrocarbons from C_{10} to C_{25} . Since the material was stored at ambient temperature (25°C), it must be assumed that these hydrocarbons have diffused to the surface of the kerogen particle from the interior of the kerogen matrix. Subsequent investigations not only corroborated this assumption but also indicated that in addition to these hydrocarbons there are entrapped within the organic matrix a number of other residual "protokerogen" components such as normal and branched fatty acids, alicyclic acids and/or their alkyl derivatives, cyclic subunits such as alkyl derivatives of decalins and tetralins, terpenoids etc. These compounds can be extracted from the matrix if one "swells" the kerogen particle by treatment with alkaline alcoholic solutions or by heat. The entrapped

fatty acids present in the matrix may explain their presence in the pyrolysate obtained under inert gas e.g. helium.

5. These experiments may indicate that these compounds may be the residual subunits from which the kerogen was formed by hetero condensation; it can be assumed that this condensation process is still progressing, although at a very slow rate, as part of the diagenetic process; however, because of the high viscosity of the substrate and the reduced diffusion rate the condensation reaction is strongly reduced. Thus a more complete structure of the isolated kerogen material could be visualized as shown schematically in Figure 4.
6. The entrapped material is very similar in composition to that of the soluble "bitumen". The latter is diffusely distributed in the oil shale between the kerogen particles and the inorganic mineral matrix. This portion of the organic matter in the oil shale of the Green River Formation may therefore also represent "protokerogen" containing material which is as yet not condensed to kerogen. Since the Green River Formation is a relatively young geologic formation it may explain the presence of the relatively high percentage (20 percent) of still soluble lower molecular weight compounds in the organic matter of the oil shale.

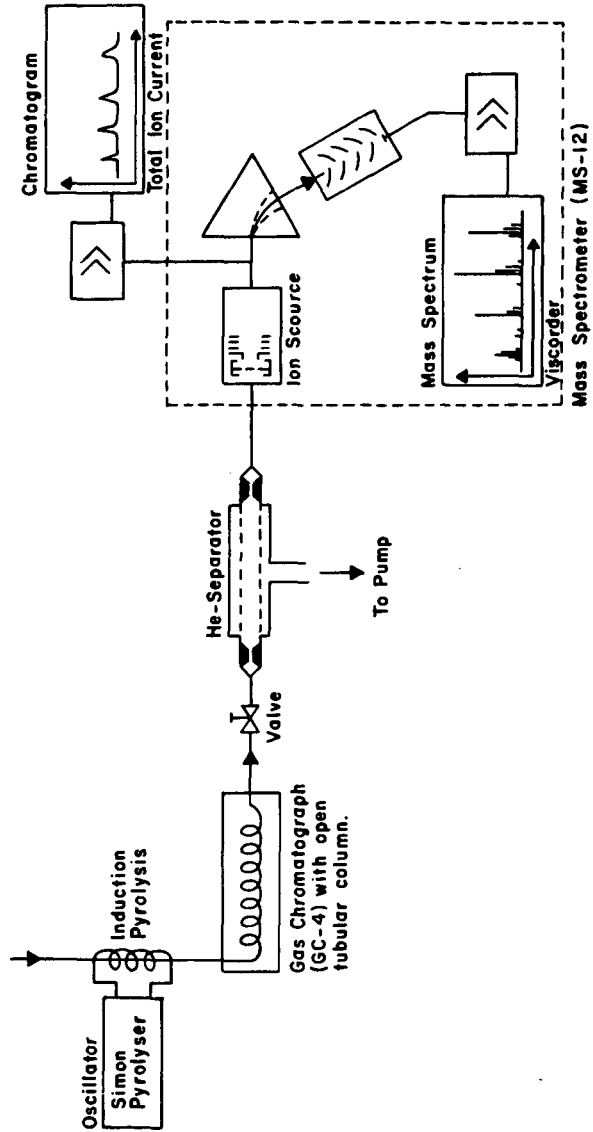


Figure 1. Schematic of the MPGM System

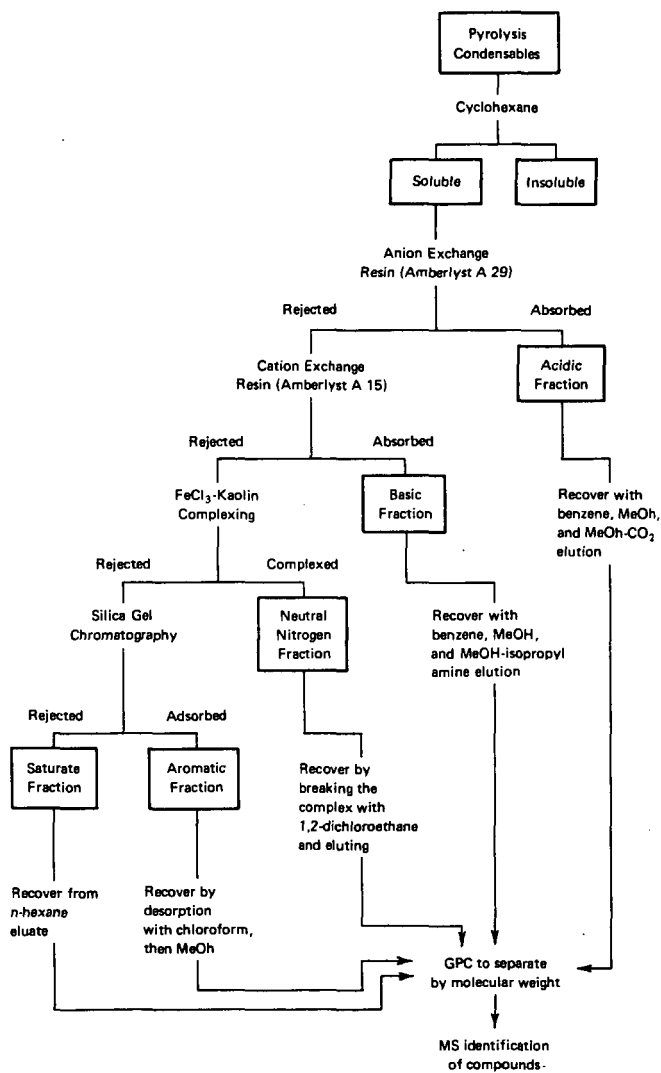

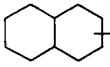
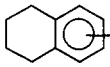
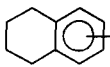
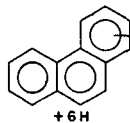

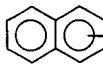
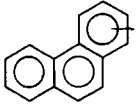


Figure 2. Separation Procedure for Pyrolysis Condensable Fraction by Functionality

Table I.

Principal Fragmentation Products of Kerogen Concentrate

No.	Name	Formula	Identified in Fraction
1	<u>Aliphatic Hydrocarbons</u>	n-C ₁₀ to n-C ₃₄	85-7
		b-C ₁₀ to b-C ₃₆	122-1
2	<u>Alicyclic Hydrocarbons</u>		
	Cyclohexanes	 C ₁₀₋₁₃ H ₂₁₋₂₇	123-1
	Decalins	 C ₅₋₈ H ₁₁₋₁₇	123-1
3	<u>Hydroaromatic Hydrocarbons</u>		
	Dialkyltetralins	 C ₂₋₅ H ₅₋₁₁	122-1 123-1
		 C ₈₋₁₂ H ₁₇₋₂₅	122-1
	Hexahydro-phenanthrenes	 C ₁₋₃ H ₃₋₇ + 6H	123-1
4	Dialkylbenzenes	 C ₈₋₁₃ H ₁₇₋₂₇	123-1
5	Dialkylnaphthalenes		123-1
			123-4
6	Alkylphenanthrenes		121-4
			123-2

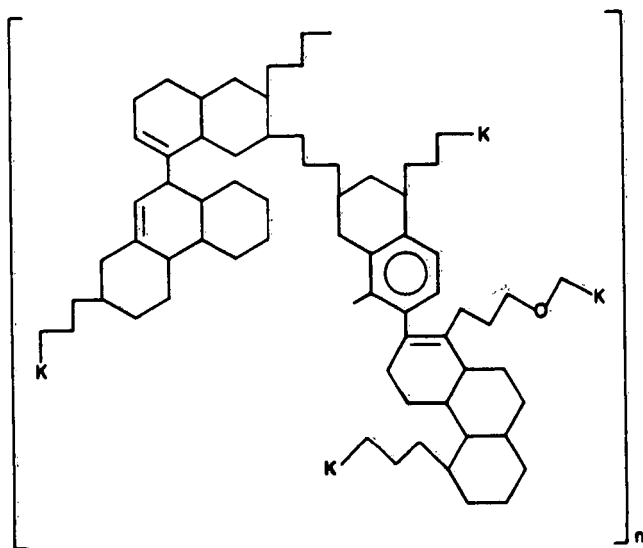


Figure 3. Generalized Structure of Kerogen of the Green River Formation

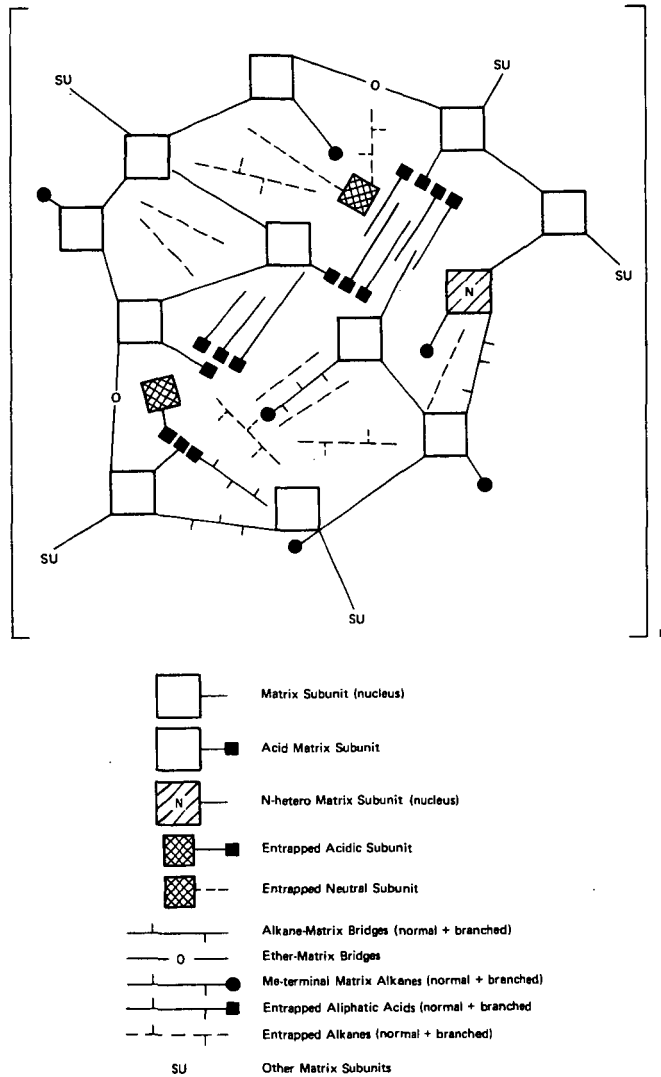


Figure 4. Schematic Structure of Kerogen Matrix